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SIMULTANEOUS GAS EVOLUTION DETECTION–DYNAMIC REFLECTANCE SPECTROSCOPY: A NEW SIMULTANEOUS THERMAL TECHNIQUE

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ABSTRACT

A DRS–GED system in which the diffuse reflectance and the gas-evolution detection curves of the same sample are recorded simultaneously is described. The new system was used to study the dehydration of $CuSO_4 \cdot 5H_2O$ and the deaquation and anation of $[Co(NH_3)_5H_2O]Cl_3$.

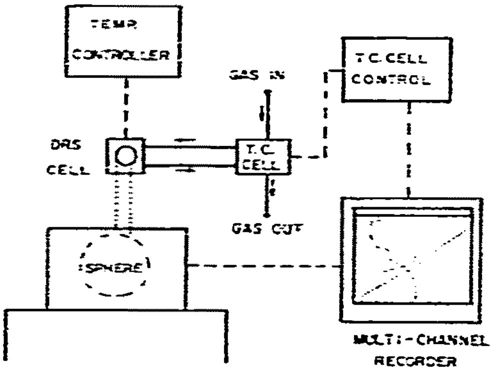
INTRODUCTION

The technique of high-temperature reflectance spectroscopy (HTRS) and dynamic reflectance spectroscopy (DRS) was first employed by Wendlandt and coworkers[1–6]. In the latter technique, the change in reflectance of the sample is recorded as a function of temperature, as the sample is heated at a slow heating rate. Several different DRS cells have been described[1,3,4,6], the latest design of which has provision for a gaseous dynamic atmosphere above the sample surface[7]. Thus, it is possible to obtain the DRS curve of a sample under rigorously controlled conditions. Because a dynamic gas atmosphere is possible in the cell, it was a simple matter to connect a thermistor type thermal conductivity cell to the system and by means of an external multi-channel recorder, record the DRS and gas evolution detection (GED) curves simultaneously.

EXPERIMENTAL

Apparatus

The DRS cell and sample holder configuration have recently been described by Wendlandt and Dosch[7]. The cell was connected to a Carle Model 100 Micro-Detector system by means of metal and rubber tubing, as shown in Figs. 1 and 2. The thermistor-type thermal conductivity cell was enclosed by an aluminum block which was heated to 100 °C by means of a cartridge heater. The block was connected to a pre-heat chamber, also operated at 100 °C, which was used to pre-heat the helium gas stream before it entered the detector. The output from the detector bridge was led into one channel of a four channel, 0–5 mV, Leeds and Northrup multi-point strip-chart potentiometric recorder. The temperature programmer from a Deltatherm III DTA instrument was used to control the temperature rise of the DRS cell[7]. Output from the Beckman Model DK-2A spectroreflectometer was also led into the multichannel recorder as well as the output from a thermocouple located in the DRS heater block.



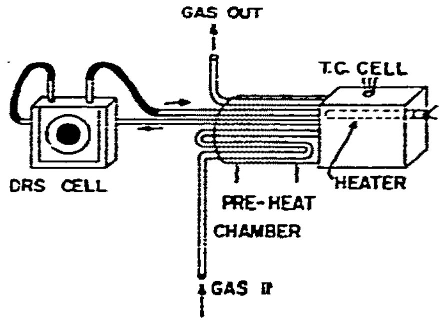


Fig. 1. Schematic diagram of DRS–GED system.

Fig. 2. Schematic diagram of DRS cell and detector system.

Procedure

From 50 to 200 mg of sample was placed into the sample indentation in the silver heater block of the DRS cell. The cell was enclosed by a glass or quartz cover plate and mounted on the sample port of the integrating sphere. The entire system was then flushed with helium gas at a flow rate of 100 ml/min for 120 min or until the recorder base line stabilized. The flow rate was then adjusted from 40–60 ml/min and the heating cycle began (usually 5 to 10°/min). Three curves were simultaneously recorded — (1) the temperature of the DRS cell, (2) the DRS curve at some predetermined wavelength, and (3) the GED curve.

RESULTS AND DISCUSSION

The DRS–GED curves of $CuSO_4 \cdot 5H_2O$ and $[Co(NH_3)_5H_2O]Cl_3$ are shown in Figs. 3 and 4, respectively.

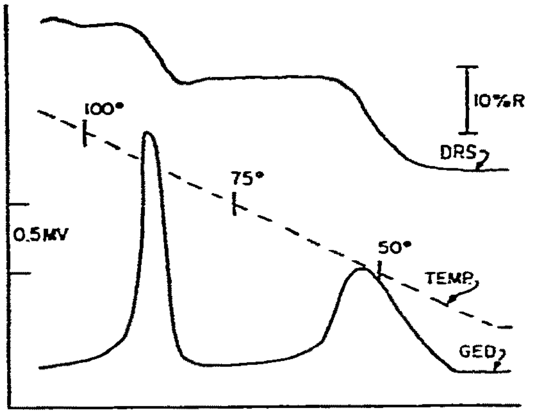
For $CuSO_4 \cdot 5H_2O$, two GED peaks were observed as well as two distinct increases in the reflectance of the sample. The first GED peak was due to the reactions[8]:

$$CuSO_4 \cdot 5H_2O(c) \rightarrow CUSO_4 \cdot 3H_2O(c) + 2H_2O(l)$$
$$2H_2O(l) \rightarrow 2H_2O(g)$$

followed by the second peak, caused by the reaction:

$$CuSO_4 \cdot 3H_2O(c) \rightarrow CuSO_4 \cdot H_2O(c) + 2H_2O(g)$$

The procedural decomposition temperatures were somewhat lower than those found by DTA or TGA but this was probably due to the large exposed sample surface and also to the pre-heating of the helium gas before entrance into the cell. The DRS curves showed two distinct increases in reflectance in the same temperature ranges as the GED peaks. Thus, dehydration of the compound resulted in a compound with a higher reflectance (lighter blue color), a result which is well known from visual observations.



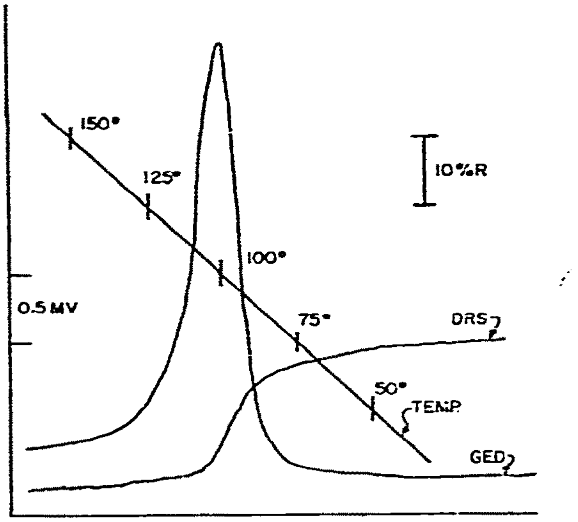


Fig. 3. DRS–GED curves for $CuSO_4 \cdot 5H_2O$; 625 nm; flow-rate of 60 ml/min; heating rate of 5°/min.

Fig. 4. DRS–GED curves of $[Co(NH_3)_5H_2O]Cl_3$; 625 nm; flow-rate of 45 ml/min; heating rate of 10°/min.

In the case of $[Co(NH_3)_5H_2O]Cl_3$, the GED curve contained only one peak while the DRS curve decreased in reflectance in the same temperature interval. The reaction involved is the deaquation and anation[1,9]:

$$[Co(NH_3)_5H_2O]Cl_3(c) \rightarrow [Co(NH_3)_5Cl]Cl_2(c) + H_2O(g)$$

Water was removed from the coordination sphere and was replaced by a chloride ion from the ionization sphere of the complex. The temperature range observed was very close to that found by DTA[9,10].

With the above combination of thermal techniques, it is possible to correlate the DRS curves with a dissociation reaction involving volatile products, a structural change in the compound, a chemical reaction not involving volatile products, or thermochromic behaviour. Unlike TGA or DTA, dynamic reflectance spectroscopy can monitor only a single reaction at a time, thus eliminating the effect of reactions occurring simultaneously[2].

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